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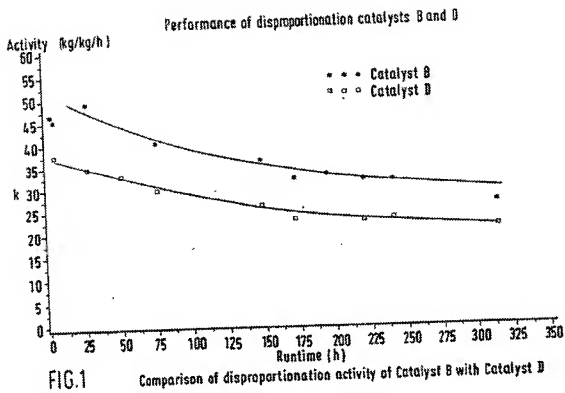
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Catalyst systems for olefin disproportionation and process using such systems.

Composition suitable as catalyst system for the disproportionation of olefins, containing molybdenum oxide supported on alumina, which composition can be obtained by commingling of at least a gamma-alumina providing agent with a sulphur containing compound and/or a phosphorous containing compound and optionally molybdenum oxide(s) or a molybdenum oxide(s) providing agent, to a homogeneous extrudable mass, extrusion of the mass and division into small particles, drying of the particles followed by calcination at a temperature in the range of from 400 °C to 800 °C, impregnating the obtained particles with a solution of a molybdenum oxide(s) providing agent and optionally with a solution of a sulphur containing compound and optionally a solution of a phosphorous containing compound, drying of the impregnated particles followed by calcination at a temperature in the range of from 400-800 °C, optionally followed by an additional impregnating step as mentioned hereinbefore, the amounts of molybdenum-, sulphur- and phosphorous containing compounds being selected such that the total final content of molybdenum is in the range of from 5 to 13% by weight, the final content of sulphur containing compound is up to 10% by weight and the final content of the phosphorous containing compound is up to 10% by weight, calculated on the weight of the total final composition.

Process for the preparation of the composition, and process for the disproportionation using the composition as catalyst.



CATALYST SYSTEMS FOR OLEFIN DISPROPORTIONATION AND PROCESS USING SUCH SYSTEMS

The invention relates to compositions suitable for use as catalyst system in a process for the disproportionation of olefins. It also relates to the preparation of such compositions and to an olefin disproportionation process in which these compositions are used as catalyst. More particularly the invention relates to an olefin disproportionation catalyst containing molybdenum oxide supported on an alumina carrier.

Such a catalyst system is known from e.g. J. Catalysis, Vol. 33, p. 83-90 (1974); J. Catalysis, Vol. 70, p. 364-374 (1981); J. Mol. Catalysis, Vol. 15, p. 157-172 and 173-185; Bull. Jap. Petroleum Institute, Vol. 18 (2) p. 162-168 (1976) Bull. Chem. Soc. Japan, Vol. 50 (4), p. 998-1002 (1977) Chemtech, Feb. 1986, p. 112-117.

In these publications research efforts are described aiming at improved olefin disproportionation selectivity by pretreatment of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst systems. This pretreatment actually consisted of the insertion of large polarizable cations such as K, Cs, Rb and Tl or addition of other copromoters, e.g. cobalt oxide, into molybdenum oxides-alumina systems and/or calcination of the initially prepared impregnated alumina carrier at varying temperatures and under varying gas atmospheres.

Varying degrees of reduction with hydrogen gas at different reduction temperatures of molybdena-alumina catalysts for the disproportionation of lower olefins, were tried to improve the disproportionation selectivity. In Japanese patent publication No. 28768-1987 a process for the disproportionation of olefins is disclosed carried out in the presence of a catalyst prepared by reducing a molybdenum tri-oxide carrying solid composite, to such an extent that the amount of the oxygen atoms is between 2.9 and 2.2 gram atoms per gram atom of molybdenum.

Recent efforts to improve the selectivity of molybdena-alumina catalysts were also directed to the activation of the catalyst by means of organo-metal derivatives, such as disclosed in Japanese patent publication No. 83043-1987 and Russian patent No. 1,264,973.

It will be appreciated that there is still a great interest in molybdena-alumina catalysts to be used in hydrocarbon chemistry, in view of the wide range of reactions in which they can be applied. During the past several years extensive research efforts continued, however without providing a fully satisfactory disproportionation catalyst system. Such a desired catalyst system has to meet the demands of modern industrial processes, for example of a process for the disproportionation of olefins. In particular of higher olefins, containing 6 to 60 carbon atoms, whereby undesired dimerisation and oligomerisation reactions are to be avoided as much as possible. Such a modern industrial process for preparing relatively narrow band predetermined fractions of olefins, e.g. containing 18-24 carbon atoms, is for example a process involving at least a double bond isomerization reaction and a disproportionation reaction.

Apparently, in spite of rather extensive research and developments efforts, those skilled in the art are still searching for alternative catalyst systems, e.g. as appears from US patent No. 3,996,168. It is an object of the present invention to provide an improved catalyst system for disproportionation of, in particular, higher olefins.

As result of research and experimentation, there was surprisingly found a composition suitable for use as a catalyst system for the disproportionation of olefins, containing molybdenum oxide supported on alumina, which composition can be obtained by commingling of at least a gamma-alumina providing agent with a sulphur containing compound and/or a phosphorous containing compound and optionally molybdenum oxide(s) or a molybdenum oxide(s) providing agent, to a homogeneous extrudable mass, extrusion of the mass and division into small particles, drying of the particles followed by calcination at a temperature in the range of from 400 °C to 800 °C, impregnating the obtained particles with a solution of a molybdenum oxide(s) providing agent and optionally with a solution of a sulphur containing compound and optionally a solution of a phosphorous containing compound, drying of the impregnated particles followed by calcination at a temperature in the range of from 400-800 °C, optionally followed by an additional impregnating step as mentioned hereinbefore, the amounts of molybdenum-, sulphur- and phosphorous containing compounds being selected such that the total final content of molybdenum is in the range of from 5 to 13% by weight, the final content of sulphur containing compound is up to 10% by weight and the final content of the phosphorous containing compound is up to 10% by weight, calculated on the weight of the total final composition.

With the term "gamma alumina providing agent" is meant any alumina starting material, which can predominantly provide the gamma-alumina phase in an irreversible way at temperatures of calcination and use of the catalyst.

The alumina starting material for the catalyst system of the present invention is preferably of the

pseudo-boehmite type, which may be represented by the formula $Al_2O_3 \cdot xH_2O$, wherein x is in the range of from 1.3 to 1.8 and which to a large extent is transformed into gamma-alumina during the preparation of the catalyst system.

Such pseudo-boehmite type aluminas may be obtained by a variety of preparation methods known in the art.

According to a more preferred embodiment of the present catalyst system, mixtures of pseudo-boehmite type aluminas are used in order to quench possible fluctuations in composition and to reach a constant purity starting material as much as possible.

Examples of suitable aluminas starting materials are commercially available Pural (Registered Trade Mark) and Versal (Registered Trade Mark) alumina powders, which are peptized with acetic acid and/or nitric acid.

Typical examples of the final catalyst systems according to the present invention, containing gamma-alumina as main ingredient, have a surface area $\geq 150 \text{ m}^2/\text{g}$, a narrow pore size distribution, an average pore diameter in the range of from 6 nm to 20 nm and a water pore volume in the range of from 0.40-0.80 ml/g.

The indicated surface areas of the gamma-alumina are all measured by the nitrogen adsorption method according to ASTM D 3663, the water pore volume and the pore diameters (by means of mercury porosimetry) have been determined as specified hereinafter.

With the term "molybdenum oxide(s) providing agent" is meant any molybdenum compound which provides molybdenum oxide(s) in the final catalyst composition under the conditions of the final calcination and/or of the use of the catalyst system for disproportionation.

In addition to MoO_3 itself, a variety of molybdenum compounds may be used, such as molybdenum carbonyl derivatives, molybdenum oxalate, molybdenum acetate, molybdenum bicarbonate, molybdenum formate, ammonium dimolybdate, ammonium paramolybdate (ammonium hepta molybdate), molybdenum sulphide and molybdenum acetyl acetonate.

It will be appreciated that molybdenum halides are not recommended for application in the present process, due to their corroding properties.

The molybdenum compounds to be applied may be used for commulling with starting pseudo-boehmite or for the impregnation of the gamma-alumina containing products by means of a solution in an organic solvent or as an aqueous solution.

Preferably ammonium dimolybdate is used, dissolved in diluted ammonia, optionally mixed with nitric triacetic acid (NTA) as complexing agent in the impregnating solution. The molybdenum oxide(s) content in the final catalyst composition calculated as to the weight thereof and expressed as molybdenum per se, will preferably be in the range of from 6-10% by weight.

With the term "phosphorous containing compound" is meant acids of phosphorous such as phosphoric acids, phosphorous acids, phosphonic acids and their salts, or mixtures thereof.

Phosphates, which may suitably be used for the preparation of the catalyst systems of the present invention may be selected from e.g. di(ammonium)hydrophosphate, tri(ammonium)phosphate, ammonium-(dihydro)phosphate, aluminium phosphate, di(sodium)hydrophosphate, di(potassium)hydrophosphate and magnesium phosphate, but also phosphorpentoxide or ortho phosphoric acid, may be used; mixtures of these compounds may also be used.

With the term "sulphur containing compound" is meant acids of sulphur and their salts, or mixtures thereof.

Sulphates which may suitably be used for the preparation of the catalyst system of the present invention may be selected from e.g. ammoniumsulphate, potassium sulphate and sodium hydrosulphate or mixtures thereof. Also sulphuric acid may be used and mixture thereof with sulphates.

The use of di(ammonium)hydrophosphate and/or ammoniumsulphate is preferred.

The amounts of sulphate and/or phosphate are normally in the range of from 0.1-10% by weight, calculated on the weight of the total final catalyst composition, and more preferably in the range of from 0.5-6% by weight.

The compositions of the present invention may be prepared by methods, in principle known per se in the art. Preferably the composition is obtained by co-mulling the starting alumina with aqueous or organic solvent solutions of the respective ingredients, to form an extrudable mass, which is extruded to a particulate mass followed by drying and calcination, whereafter the obtained particles are impregnated with a solution of an (additional) molybdenum oxide(s) providing agent and optionally one or more of sulphur containing and/or phosphor containing ingredients, followed by drying and calcination.

It will be appreciated that the complete impregnation, drying and calcination step may be carried out in one or more steps and that e.g. in a first step molybdenum oxide(s) or molybdenum oxide(s) providing

agent(s) may be incorporated while in a second step the sulphur containing compound and/or phosphorous containing compound is incorporated or vice versa.

Preferably the impregnation and subsequent drying and calcination of all ingredients will be carried out in one sole step.

- 5 It will be appreciated that the finished catalyst can be in the form of extrudates (e.g. cylindrical, trilobed, quadrilobed and hollow extrudates) as well as in the form of other shapes such as agglomerates, pellets, spheres, beads and will be depending upon the type of contacting technique which utilizes the catalyst.

The first calcination step after commingling and shaping is preferably carried out at a temperature in the range of from 500 to 750 °C.

- 10 A period in the range from 1 to 20 hours and more preferably of from 2-10 hours is applied for this first calcination. Calcination of the impregnated particles is preferably carried out at temperatures between 450 °C and 750 °C.

For this calcination a period of at least one hour and preferably a period in the range of from 2 to 10 hours is used.

- 15 The pore diameters of the catalysts of the present invention, as indicated throughout the specification, were measured by mercury porosimetry in the following way:

A calibrated penetrometer, containing a weighed amount of sample, whose interior pores have been completely freed from moisture by heating at elevated temperature, is evacuated and subsequently filled with mercury. Under increasing hydrostatic pressure mercury is forced into the open pores of the sample.

- 20 The volume of mercury intruded into the pores by an applied intrusion pressure is calculated from the measured change of the level of mercury in the capillary of the penetrometer and the diameter of the capillary. The pore diameter is derived from the measured intrusion pressure, surface tension of mercury and contact angle between mercury and the sample using the Washburn equation for cylindrical pores:

$$25 \quad \text{Pore diameter} = \frac{-4 \cos \theta}{P}$$

where γ = surface tension of mercury

θ = contact angle between mercury and sample

- 30 P = hydrostatic intrusion pressure.

The pore diameter distribution can be defined from either the cumulative of volume changes or from incremental volume changes with decreasing pore diameter.

It will be appreciated that

- (a) The intrusion volume at any value of applied pressure gives the volume of all pores having a 35 diameter equal to or greater than the calculated diameter.

(b) Taking $\theta = 141.30^\circ$, and $\gamma = 0.4805 \text{ Nm}^{-1}$. The Washburn equation becomes

$$\text{Pore diameter (d)} = \frac{4\gamma}{P}$$

where, if we assume d is expressed in nm, the constant K1 takes the values:

$$1.471 \times 10^6 \text{ if } P \text{ is in kPa}$$

- 40 $1.451 \times 10^4 \text{ if } P \text{ is in atm}$

$$1.500 \times 10^4 \text{ if } P \text{ is in dg/cm}^2$$

The maximal pressure $P = 80.000 \text{ psi}$ (pores down to 4 nm).

- The water pore volume of the catalysts as indicated throughout this specification, was determined 45 according to the methods, described in principle in "Introduction to characterization and testing of catalysts", J.R. Anderson and K.C. Pratt, Academic Press Australia, 1985 and adapted in the following way: As the water pore volume depends on the moisture content of the sample, this has to be previously calcined. Thereof, the sample is heated in one hour to 500 °C and kept one hour at this temperature.

- Subsequently the sample is cooled down for one hour in an exsiccator, whereafter the actual 50 measurement is carried out as soon as possible. 25 g of the calcined catalyst is weighed out to a precision of 1 mg and is transferred into a dry wide-mouthed flask of 100 ml. From a burette an amount of water is added to the sample, corresponding with 90% of the expected pore volume and the flask is accurately stoppered.

- The flask is agitated for 20 seconds and is allowed to cool down, if necessary, by placing it on a 55 waterbath on ambient temperature for 10 minutes. The flask is dried and is shaken for 5 seconds.

0.2 ml portions of water are added stepwise. After every addition, the flask is shaken vigorously, 10 times vigorously tapped on a hard underground and immediately thereafter turned upside down carefully. If the material is no longer free flowing but is sticking to the flask wall in such a way, that the bottom remains

almost completely covered for two seconds or longer the endpoint is reached. If the result is doubtful, the shaking and vigorously tapping is repeated. The time period for the determination has to be about 15 minutes. When the determination requires a shorter period, the endpoint has to be checked at 15 minutes after the start of the titration.

- 5 if the end point is then not reached, the stepwise addition of water, shaking and tapping the flask and turning upside down the flask is repeated and checking is repeated after 15 minutes again. This procedure is continued until the endpoint is reached. The water pore volume of the dried material is calculated by the equation:

$$PV \text{ H}_2\text{O (ml/g)} = \frac{W}{V} \text{ wherein } V = \text{volume of the added water in ml, } W = \text{weight of the sample in g.}$$

- 10 It will be appreciated that suitable compositions embraced by the scope of the present invention may also be obtained by impregnation of a semi-manufactured particulate product produced under the previously defined conditions, containing already the sulphate and/or phosphate or a part of the desired final amounts thereof and optionally a part of the desired final molybdenum amounts, with a molybdenum oxide providing agent to obtain a catalyst system with the desired final molybdenum amount and calcination of the impregnated product under the hereinbefore indicated conditions.

15 According to a most preferred embodiment of the present invention the catalyst is prepared by impregnation of a γ -alumina carrier, which contains 3-8% by weight molybdenum and 2% by weight phosphate previously introduced by commingling, with 3-6% by weight molybdenum, calculated as MoO_3 .

- 20 Before the actual use of the composition as catalyst for the disproportionation process, it is activated according to a preferred embodiment at a temperature in the range of from 400-800 °C and more preferably at a temperature in the range of from 550-725 °C under nitrogen for 5-20 hours.

The catalyst systems of the present invention show a significantly improved activity and selectivity as to disproportionation, reaching at least 95% as to linear olefins, whereas the dimerization and oligomerisation appear to be significantly reduced as compared to prior art catalysts.

- 25 The catalyst systems have shown more particularly to be suitable for disproportionation of the relatively higher olefins, containing 6-60 carbon atoms.

The disproportionation may be carried out either batchwise or continuously using a fixed catalyst bed or a fluidized catalyst bed or any other mobile catalyst contacting process. Preferred reaction conditions of the disproportionation process e.g. temperature, pressure flow rates etc. may vary somewhat depending upon the specific catalyst composition, the particular feed olefin, desired products etc. The process is typically carried out at temperatures in the range of from 75 to 250 °C and under a pressure in the range of from 1 to 50 bara. More preferably a temperature in the range of from 100 to 150 °C is used.

- 30 Although the olefin reactions according to this invention are rather independent of the pressure, for most economical operation considering combination with other steps of a complete plant operation including for example, product separation and recovery, a pressure range of from 5 to 25 bara can be used conveniently.

It will be appreciated that the catalysts according to the present invention show the advantage, that due to their improved stability, process economics are improved because less regenerations and change out of the catalyst are required than in processes carried out under industrial conventional operation conditions. Moreover due to a better selectivity reduced cycle streams are adequate, which also improves the process economy.

- 40 The invention is further illustrated by the following examples, however, without restricting its scope to these embodiments.

45 Preparation of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts

Example 1

- 50 1036 g of a commercial alumina (HDS-base, Katjan, Registered Trade Mark), containing 2% by weight sulphate, based on the weight of the calcined composition, was mixed in a Lancaster kneading equipment with 434 g water and 300 g acetic acid (5% by weight). After kneading for 45 minutes a mix is obtained which is extruded subsequently in a Bonnot single screw extruder and the obtained extrudate was dried at 120 °C for 2 h and subsequently calcined for 2 h at 560 °C.

- 55 80 g of this particulate product, mainly consisting of gamma-alumina and showing a water pore volume of 0.59 ml/g was dried at 450 °C for 1 h and impregnated with a solution, derived from 28.7 g ammonia (25.5% by weight) and 12.69 g ammonium dimolybdate in about 10 ml of demineralized water, whereafter the total volume was adjusted to 47 ml with demineralized water, by mixing the mass in a rolling flask for 1

- h. Thereafter the obtained mass was dried with an airblower for 5 h at a maximal temperature 63 °C. Subsequently the mass was heated in an oven up to 120 °C, was kept on this temperature for 2 h and heated up to 725 °C in 2 h, at which temperature it was kept for 1 hour.
- The obtained catalyst contained an amount of molybdenum corresponding with 12% by weight MoO₃, based on the weight of the final catalyst system (A), having a surface area of 310 m²/g.

Example 2

- In a Lancaster mix miller were mixed together 1036 g of Keljen HDS base (Registered Trade Mark) containing 2% by weight sulphate, 18.0 g acetic acid (3%) and 38.3 g MoO₃ (Murax, Registered Trade Mark) and 52.2 g water and the mass was kneaded during 45 minutes. The obtained paste was extruded by means of a Bonnot extruder (Registered Trade Mark) with a 1.8 mm Delrin (Registered Trade Mark) mold having 54 holes.

The extruded mass was dried at 120 °C for two hours and calcined at 580 °C for 2 hours.

- 100 g of the calcined product, containing as main ingredient gamma-alumina, 4% by weight molybdenum (6.0% by weight of MoO₃) and 1.9% by weight of sulphate (calculated on the weight of the total calcined composition) having a water pore volume of 0.71 ml/g, was dried at 300 °C for 18 hours and impregnated with a solution, derived from 35.04 g ammonia (25.5% by weight), 20.04 g demineralized water, 8.08 g ammonium dimolybdate and addition of water up to a volume of 70.5 ml. After impregnation the mass is equilibrated for 1 hour.

- Thereafter the obtained mass was dried with an airblower for 5 hours to a temperature of 83 °C and subsequently placed in an oven and heated in an oven up to 120 °C. The mass was kept at this temperature for 2 hours and subsequently heated up to 725 °C over two hours and kept at this temperature for 1 hour.

- The obtained catalyst contained 12.0% by weight of MoO₃, based on the weight of the final catalyst system (B), showing a surface area of 269 m²/g, a pore volume of 0.58 ml/g, an average pore diameter of 8.8 nm.

Example 3

- In a Lancaster mix miller were mixed together 529 g of Kaiser Versal 250 (Registered Trade Mark), 539 g of Condea Pural SB (Registered Trade Mark), 24 g acetic acid (3% by weight), 22.3 g (NH₄)₂HPO₄, 51.1 g MoO₃ and 813 g water, whereby the obtained mass was kneaded during 0.55 hour in total.

The paste was extruded through a Delrin (Registered Trade Mark) dieplate, having 54 holes having a diameter of 1.8 mm.

The extruded mass was dried at 120 °C for two hours and calcined at 580 °C for two hours.

- 100 g of the so obtained product, consisting of gamma-alumina as main ingredient and containing 4% by weight Mo (6% by weight MoO₃) and 2% by weight phosphate, and having a water pore volume of 0.71 ml/g, was calcined at 450 °C for 1 hour and subsequently impregnated with a solution derived from 34.13 g ammonia (25.5% by weight), 20.06 g demineralized water and 8.04 g ammonium dimolybdate (56.4% Mo) and added water up to 71 ml.

- Thereafter the obtained mass was heated in an oven in the same way as previously described in examples 1 and 2.

The obtained catalyst contained 11.99% by weight MoO₃, based on the weight of final catalyst system (C), showing a surface area of 257 m²/g, a pore volume of 0.58 cm³/g, an average pore diameter of 9.6 nm.

Example 4

In exactly the same way as described in example 3, a catalyst (F) was prepared except that the final calcination temperature was 450 °C.

Example 5

The catalyst systems hereinbefore identified by A, B, C were tested as to disproportionation activity after activation at a temperature of 550 °C under air for 5 h and subsequently under nitrogen for 15 h in the following way.

In the test method an activated catalyst is exposed to purified and fully isomerized model test feed (C₁₂ olefins) in a recirculation system.

The procedure avoids any contact of the activated catalyst with oxygen during its transport from the furnace to the recirculation system.

The performance of the activated catalyst is subsequently measured by circulating the test feed (350 ml) over the catalyst (25 grammes) at the rate of 10 l.h⁻¹ and at 125 °C. At regular intervals samples are taken in such a way that loss of light products is avoided.

In this closed recirculation system used, loss of light products produced in the disproportionation reaction is negligible. In this way the dimer make by the catalyst at any time during the test can be determined by calculating the decrease of the number of moles in the reaction product.

The rate of disproportionation can be determined from the decrease of the concentration of the test feed (C₁₂) with progressing reaction time. The data obtained suggest that the disproportionation reaction can be described by a (pseudo) first-order reversible reaction.

This means that for the beforedescribed screening test the following formula can be used for the disproportionation activity and dimerization activity.

$$kt = \frac{OW}{CW} \cdot \ln \frac{1}{1 - \text{fraction } C_{12} \text{ converted}}$$

wherein k represents the first order disproportionation rate constant
OW represents the weight of the olefin at time period t
and CW represents the weight of the catalyst

$$\frac{M_o - M_t}{M_o} \times 100\%$$

wherein M_o represents the number of olefin moles in feed
M_t represents the number of olefin moles in product after time period t, respectively.

The obtained results with the catalyst samples A, B, C and with two commercially applied catalyst compositions (D and E) have been summarized in the following table.

TABLE

Exp. No.	Catalyst	Metal oxide %w MoO ₃		Anion %w			Final Calcin. temp. °C	Disprop. Rate constant 'k' kg.kg ⁻¹ .h ⁻¹	Dimer make % mol %
		commuted	impregn	CoO	SO ₄	PO ₄			
1	A	-	12		2		725	52	4.7
2	B	6	6		2		725	55	4.4
3	C	6	6			2	725	46	3.1
4	D	-	12	4	2		?	30	5.2
5	E	-	15	4			675	30	7
6	F	6	6				450	41	4.2
D = industrially used disproportionation catalyst obtained by impregnation with MoO ₃ and CoO of a support as prepared in Examples 1 and 2. E = Commercially used disproportionation catalyst as described in GB 1,117,968 (without molecular hydrogen).									

Example 3

In a continuous experiment for testing the stability, the performance of catalyst B has been compared with that of catalyst D. C₁₂ isomerised in situ in an isomerisation reactor prior to both disproportionation reactors was used as feed.

The test reactor was operated at an operational pressure of 5-10 bar, a temperature of 126 °C and the WHSV was in the range of 2.2-3.5 kg/kg/h. At regular intervals the WHSV was increased to 10-12 kg/kg/h to determine the activity of the catalysts to be tested, and thus its deactivation rate. The obtained results with both catalysts have been depicted in fig. 1. The disproportionation reaction is also here described, as in Example 5, by a (pseudo) first order reaction, and the results are presented by the first order disproportionation rate constant k.

$$k = \text{WHSV} * \ln \left[\frac{1}{1-x} \right], \text{ where}$$

$$x = \frac{C_{12}(o) - C_{12}(e)}{C_{12}(o) - C_{12}(e)}$$

wherein

C₁₂(o) represents C₁₂ concentration in the feed,

C₁₂(t) represents C₁₂ concentration in the product at time = t,

C₁₂(e) represents C₁₂ concentration in the product at equilibrium of the disprop. reaction (i.e. at low WHSV).

Claims

1. Composition suitable as catalyst system for the disproportionation of olefins, containing molybdenum oxide supported on alumina, which composition can be obtained by commingling of at least a gamma-alumina providing agent with a sulphur containing compound and/or a phosphorous containing compound and optionally molybdenum oxide(s) or a molybdenum oxide(s) providing agent, to a homogeneous extrudable mass, extrusion of the mass and division into small particles, drying of the particles followed by calcination at a temperature in the range of from 400 °C to 800 °C, impregnating the obtained particles with a solution of a molybdenum oxide(s) providing agent and optionally with a solution of a sulphur containing compound and optionally a solution of a phosphorous containing compound, drying of the impregnated particles followed by calcination at a temperature in the range of from 400-800 °C, optionally followed by an additional impregnating step as mentioned hereinbefore, the amounts of molybdenum-, sulphur- and phosphorous containing compounds being selected such that the total final content of molybdenum is in the range of from 5 to 13% by weight, the final content of sulphur containing compound is up to 10% by weight and the final content of the phosphorous containing compound is up to 10% by weight, calculated on the weight of the total final composition.

2. Composition according to claim 1, characterized in that it has a surface area of $\geq 150 \text{ m}^2/\text{g}$, a narrow pore size distribution, an average pore diameter in the range of from 6 nm to 20 nm and a water pore volume in the range of from 0.40 to 0.80 ml/g.

3. Composition according to claim 1 or 2, characterized in that it is derived from alumina starting material of the pseudo-boehmite type, which may be represented by the formula $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, wherein x is in the range of 1.3 to 1.8.

4. Composition according to any one of claims 1-3, characterized in that the molybdenum oxide(s) content in the final composition, expressed as molybdenum per se, is in the range of from 6-10% by weight.

5. Composition according to any one of claims 1-4, characterized in that the amounts of sulphur containing compound and/or phosphorous containing compound are in the range of from 0.5-6% by weight, calculated on the weight of the total final composition.

6. Composition according to any one of claims 1-5, characterized in that the final composition is in the form of cylindrical, trilobe, quadrolobe or hollow extrudates.

7. Process for the preparation of a composition according to claim 1, characterized in that at least a gamma-alumina providing agent, is commulled with a sulphur containing compound and/or phosphorous containing compound and optionally molybdenum oxide(s) or a molybdenum oxide(s) providing agent to a homogeneous extrudable mass, followed by extrusion of the mass and division into small particles, drying of the particles, calcination at a temperature in the range of from 400 °C to 800 °C, impregnating the obtained particles with a solution of a molybdenum oxide(s) providing agent and optionally a solution of a sulphur containing compound and optionally a solution of a phosphorous containing compound, drying of the impregnated particles and calcination at a temperature in the range of from 400-800 °C for at least 1 hour, optionally followed by an additional impregnating step as mentioned hereinbefore, the amounts of molybdenum-, sulphur- and phosphorous-containing compounds being selected such that the total final content of molybdenum is in the range of from 5-13% by weight the final content of sulphur containing compound is up to 10% by weight and the final content of phosphorous containing compound is up to 10% by weight, calculated on the weight of the total final composition.
8. Process according to claim 6, characterized in that as molybdenum compound ammonium dimolybdate is used, dissolved in diluted ammonia, optionally mixed with nitrilo triacetic acid as complexing agent.
9. Process according to claim 7 or 8, characterized in that as the phosphorous containing compound phosphor pentoxide, ortho phosphoric acid or di(ammonium)hydrophosphate is used.
10. Process according to any one of claims 7-9, characterized in that as sulphur compound ammonium sulphate is used.
11. Process according to any one of claims 7-10, characterized in that the first calcination step after commulling is carried out at a temperature in the range of from 500-750 °C.
12. Process according to any one of claims 7-11, characterized in that the first calcination step after commulling is carried out for a period in the range of from 2 to 10 hours.
13. Process according to any one of claims 7-12, characterized in that the calcination of the impregnated particles is carried out at temperatures between 450 °C and 750 °C for a period in the range of from 2 to 10 hours.
14. Process according to any one of claims 7-13, characterized in that the composition is activated for use as catalyst in the disproportionation of olefin by heating at a temperature in the range of from 550-725 °C under nitrogen for 5-20 hours.
15. Process for the disproportionation of olefins containing 6-60 carbon atoms characterized in that a composition according to any one of claims 1-6 is used as catalyst system.

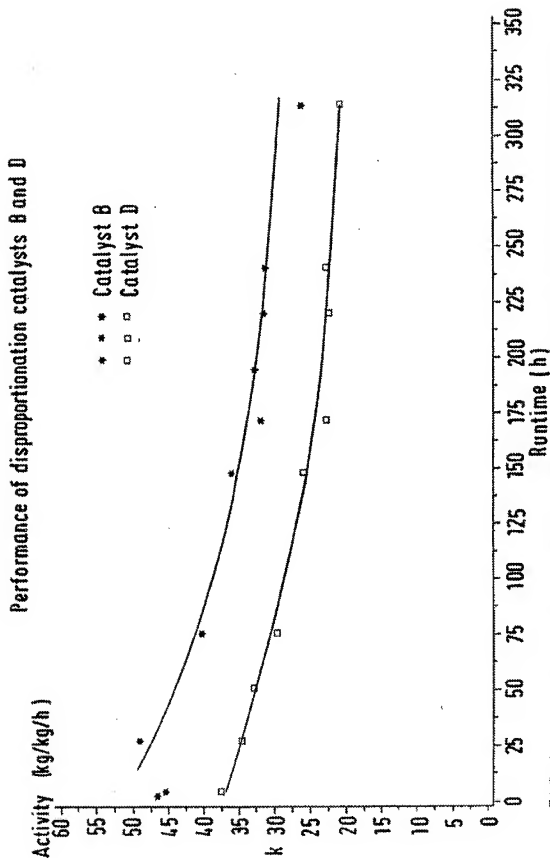


FIG.1 Comparison of disproportionation activity of Catalyst B with Catalyst D



European Patent
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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 201 949 (SHELL) ----		B 01 J 27/19 B 01 J 27/188
A	US-A-4 560 466 (S.G. KUKES) ----		B 01 J 27/053 C 07 C 6/04
A	US-A-4 003 828 (P.E. EBERLY) ----		
A	FR-A-2 010 569 (SHELL) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			B 01 J C 07 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-03-1989	Examiner THION M. A.
CATEGORY OF CITED DOCUMENTS		I : theory or principle underlying the invention E : earlier patent document, sui published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : non-written disclosure P : intermediate document	
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